

Adsorption Study of Some Heavy Metal Ions on Modified Kaolinite Clay

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ABSTRACT:

A laboratory batch study has been performed to study the effect of various physic-chemical factors such as the initial metal ion concentration, the solution's pH and the contact time on the adsorption characteristics of mercury (Hg^{2+}), lead (Pb^{2+}) and cadmium (Cd^{2+}) ions onto kaolin and its acid and alkali treated. It has been found that the amount of adsorption of metal ions increases with (directly proportional?) initial metal ion concentration, contact time and solution's pH. Kinetic experiments clearly indicate that adsorption of metal ions on untreated and treated kaolin is a two steps process: a very rapid adsorption of metal ions to the external surface is followed by possible slow decreasing intra-particle diffusion in the interior of the adsorbent. The equilibrium time in the order is found to be of 60 min. The adsorption capacity of kaolin and modified kaolins for metal ions was as follows: $Hg^{2+} > Pb^{2+} > Cd^{2+}$. Overall the kinetic studies showed that the adsorption process followed the pseudo-first-order. The different kinetic parameters including rate constant were determined. The equilibrium adsorption results were analyzed by both Langmuir and Freundlich models to determine the mechanistic parameters associated with the adsorption process. The value of the separation factor, R_L from Langmuir equation also gives an indication of favorable adsorption.

KEY WORDS: Kaolin, modification, adsorption, heavy metals, kinetics

I. INTRODUCTION

Kaolin clay is widely used for a large number of applications. Kaolinite is the major mineral component of kaolin, which usually may contain minor minerals such as quartz and mica [1-2]. Kaolin is a 1:1 layer sheet of structured hydrated aluminum silicate with a very fine particle size with one silicon oxygen (SiO_4) tetrahedral layer and one alumina [$Al(O, OH)_6$] octahedral layer. It has a formula of $Si_2Al_2O_5(OH)_4$ or $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ [2-4].

The industrial utilization of kaolinite is closely related to its reactivity and surface properties, which depend strongly on surface modification. Several methods have been suggested in literature to improve the properties of clay materials which include among others mechanochemical activation [5-15], intercalation [16-18], thermo-chemical treatment [1,2, 19-21] and chemical activation [22-24].

Kaolin is safe, environmentally friendly, naturally occurring minerals that are aluminosilicates and have an open box work crystal structure which is occupied by cations and water molecules. These ions and water molecules can move within the large cavities allowing ionic exchange and reversible rehydration.

Acid activation has been widely studied as a chemical treatment method for the improvement of the surface and catalytic properties of fibrous clays (sepiolite and palygorskite), smectite clays (saponite and montmorillonite) [1] and amorphized (calcined/grounded) kaolin [1,3,4,12-15,25]. The method involves leaching of the clays with inorganic acids, causing disaggregation of clay particles, elimination of mineral impurities, and dissolution of the external layers, thus altering the chemical composition and the structure of the clays.

The acid treatment is beneficial in terms of increased surface area, porosity and number of acid centers with respect to the parent clays. The acid treated clays are composed of a mixture of non-attacked clay layers and a hydrous, amorphous, and partially protonated silic phase. These high surface area silica gels are competitive in different industrial uses and very promising as sorbents or as catalyst supports [1].

The solubility of kaolinite in acids varies with the nature and concentration of the acid, the acid-kaolinite ratio, the temperature, and the duration of treatment. The kaolinite is more soluble in sulfuric than in hydrochloric acid [26].

The wastewater purification processes require the development of new operations based on low-cost raw materials with high pollutant-removal efficiency. Many toxic heavy metals are being discharged into the environment as industrial wastes, causing serious soil and water pollution [27]. Heavy metals such as zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni) and copper (Cu) are prior toxic pollutants in industrial wastewater, which become common groundwater contaminants and they tend to accumulate in organisms, causing numerous

diseases and disorders [28]. The complexity of effluents makes the process of heavy metals removal more difficult due to presence of organic legends, phosphate, cyanide and humic matter that can be added to complexity of removal, as well as strict limitations that have been imposed to wastewater discharge everywhere in aquatic recipients [29].

The objective of the present study is to investigate the performance and capacity of modified kaolin in removal of heavy metals.

II. EXPERIMENTAL

2.1. Adsorbent preparation

The kaolinite clay was collected from Wadi Kalabsha holding around 17 million metric tones, is situated at about 150 km of west of Aswan, Egypt. Kaolinite clay sample was prepared through attrition scrubbing followed by magnetic separation to separate the iron content then froth flotation to separate the anatase impurities (TiO₂).

2.2. Modification of adsorbent

A portion of 200 g of kaolinite clay was added to 500 ml of 1 mol/l NaOH solution for alkaline treatment or 1 mol/l (KH₂PO₄/H₂SO₄) solution for acid treatment. The latter was stirred for 24 h at a room temperature of 27°C. The aqueous phase was decanted and the residue washed with excess bi-stilled de-ionized water to neutralize the pH. The clay was oven-dried at 100°C for 24 h then pulverized and passed through a mesh sieve of size 200 mesh, (74 µm) to obtain alkaline or acidic modified kaolinite clay. The adsorbent was stored in a glass bottle for further use.

2.3. Characterization of adsorbents

The chemical composition of the clays was characterized by atomic absorption spectrophotometry, Perkin Elmer, Model AAnalyst 200, after digestion with nitric and hydrofluoric acid. The surface areas of the clay adsorbents were estimated following Sears' method [30]. A sample containing 0.5 g of clay was acidified with 0.1 N HCl to pH 3 to 3.5. The volume was made up to 50 ml with distilled water after an addition of 10g of NaCl. The titration was carried out with standard 0.1 M NaOH in a thermostatic bath at 298 ± 0.5 K to pH 4.0, and then to pH 9. The volume, V, required to raise the pH from 4 to 9 was noted and the surface area was computed from the following equation:

$$\text{Surface area (m}^2\text{/g)} = 32 V - 25.$$

The X-ray diffraction of the adsorbents was determined by the X-ray diffractometer (Bruker, Darmstadt, Germany). X'PERT PRO MPD, with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The pore properties and Brunauer, Emmett and Teller (BET) surface area of the adsorbents were determined from nitrogen adsorption-desorption isotherms in a micrometrics accelerated surface area and a porosimetry system 2010 model analyzer.

2.4. Batch adsorption

The adsorption experiments were carried out in 100 ml Erlenmeyer flasks by 0.1 gram adsorbent clay with 50 ml of the aqueous solution of heavy metal ions. The contents in the flask were agitated by placing them in a constant temperature water bath thermostat for a known time interval. The mixture was then centrifuged and the metal ions (Hg²⁺, Pb²⁺ or Cd²⁺) remaining unadsorbed in the supernatant liquid was determined with Atomic Absorption Spectroscopy (Perkin Elmer, Model AAnalyst 200). The pH of the adsorptive solution was adjusted by the addition of either 0.01 N NaOH or 0.01 N HCl.

III. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

Mineralogical and geochemical investigations indicated that these deposits are composed of kaolinite with traces of quartz and that they are of a detrital origin. Iron and titanium occur as ilmenite and anatase in very fine grains as rhombs and net structure. No iron and titanium were found in the structure of the kaolinite. Table 1 shows the complete chemical analysis of the purified kaolinite clay sample.

Table 1: Complete chemical analysis of the purified kaolinite clay sample.

Constituents	%
SiO ₂	52.6
Al ₂ O ₃	34.4
Fe ₂ O ₃	0.25
TiO ₂	0.75
CaO	0.21
MgO	0.13
Na ₂ O	0.17
K ₂ O	0.08
Cl ⁻	0.04
L.O.I.	11.35
Total	99.98

The specific surface area of kaolinite, alkali and acid activated kaolinite is measured as 16.2, 82.5 and 159.3 m²/g, respectively. No report on the effect of acid treatment on the specific surface area of kaolinite could be found, but the untreated kaolinite is reported to have specific surface area of 5 to 25 m²/g [31]. The acid treatment opens up the edges of the platelets and as a consequence, the surface area and the pore diameter increase [32].

Fig.1 shows the XRD profiles of the untreated and treated kaolins. The parent clay shows well-defined reflections at 2θ values of 12° and 25° (corresponding to the d values of 7.154 and 3.575) which are the typical characteristic peaks of kaolinite. Again the peaks corresponding to the 2θ values 34–36°, 38–42° and 45–50° are also characteristic of kaolinite [33]. Upon acid treatment the peak intensity of the clay was found to be decreasing progressively. This is due to the structural disorder that occurred owing to the acid treatment, which affects the crystalline character of the clay [34]. The narrowing of the peak may be related to the increase of the crystallite size and/or the decrease of the mean lattice strain [35].

On the other hand, the sharp increase in the intensity of the montmorillonite peak in alkaline-modified clay suggests that the leached silica came from the silica phase and not the montmorillonite phase. XRD gave useful information about crystalline and amorphous changes of an adsorbent. The presence of sharp and weak peaks suggests that it is an amorphous adsorbent [36], and the amorphous nature of alkaline-modified clay indicates that the metal ions in the solution can easily penetrate its surface for efficient adsorption [37-38].

3.2. Adsorption Study

3.2.1. Effect of pH

The initial pH of a solution is an important parameter in adsorption, as metal ion removal usually increases with increasing pH. The pH of a solution affects the degree of ionization of the adsorbate and the surface properties of the adsorbent. The effect of initial pH of the solution on the percentage removal of metal ions onto alkaline-modified clay is shown in Fig.2. Adsorption of both metal ions increased with increasing pH, with significant adsorption at pH 6–7, which is higher than the zero point of charge of 5.2 of alkaline-modified clay as the surface became negative. An optimum pH of 6 was selected and used for all experiments in order to avoid the formation of metal hydroxide precipitates at higher pH. At lower pH, higher concentrations of H⁺ ions are present in solution, which creates a competition between the protons and the metal ions for the active sites of the adsorbent. The lower adsorption at low pH was thus due to saturation of the active sites of alkaline-modified clay with hydrogen ions. The increased removal of metal ions with increasing pH is also due to a less competition between the protons and the metal ions for the active sites and a decrease in the positive surface charge, which results in less electrostatic repulsion between the surface and the metal ions before the ion exchange [39]. Acid-modified clay had a higher adsorption capacity than the alkaline-modified ones for all metal ions. The modified clays had a higher adsorption capacity than unmodified clay indicating the effectiveness of the modification. The higher adsorption by acid-modified clay may be due to its increased surface area. The moderate adsorption by alkaline-modified clay may be due to a better cation exchange capacity as compared with unmodified kaolin clay.

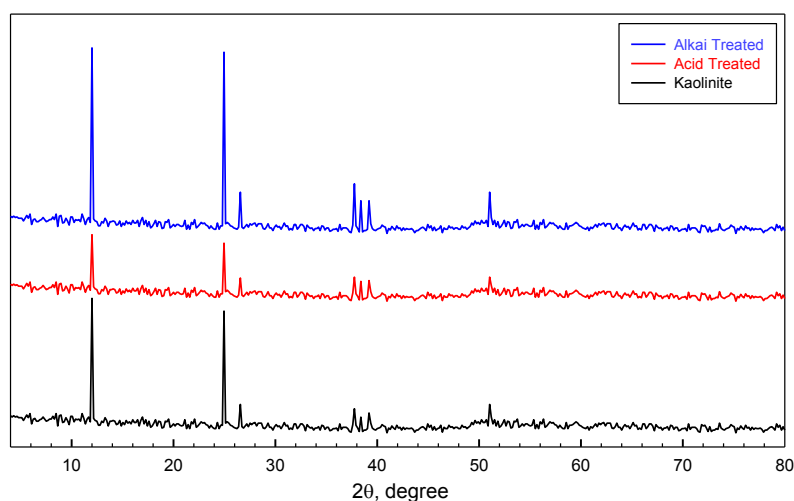


Fig.1. X-Ray Diffraction spectra of the untreated and treated kaolins.

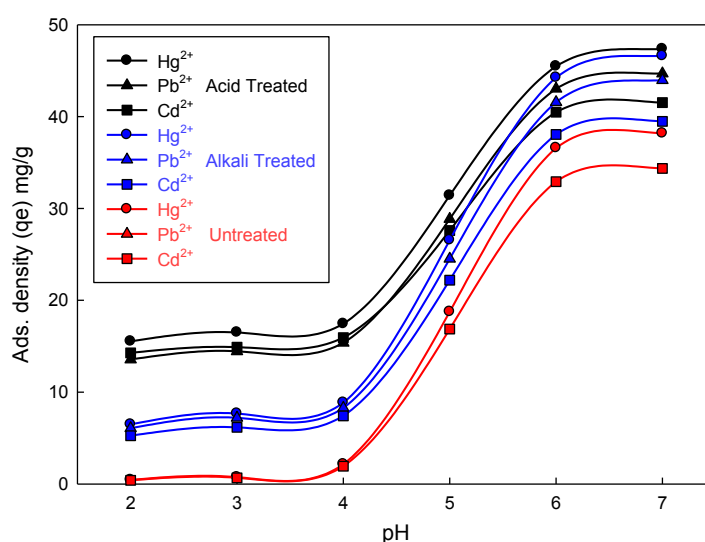


Fig.2. Effect of pH on metal ions adsorption onto untreated and treated kaolins.

3.2.2. Effect of contact time

The effect of contact time on the adsorption of metal ions onto modified kaolin clay is shown in Fig.3. Equilibrium removal was achieved around 60 min for all metal ions after which further increases in contact time did not result in significant adsorption. Thus, 60 min was used in all experiments to ensure the maximum removal. The rapid adsorption during the initial stages might be due to the presence of abundant active sites on the surface of the kaolin clay, which becomes saturated with time. Initially, sorption is controlled mainly by diffusion from the bulk to the surface of the clay; whereas, sorption is probably an attachment-controlled process due to the presence of fewer active sites [17]. The experimental results indicated that the order of the adsorption capacity of kaolin and modified kaolins for metal ions was as follows: $Hg^{2+} > Pb^{2+} > Cd^{2+}$. These results may be due to that the fluctuation motion of $Hg^{2+} > Pb^{2+}$ and that which is greater than Cd^{2+} [40, 41].

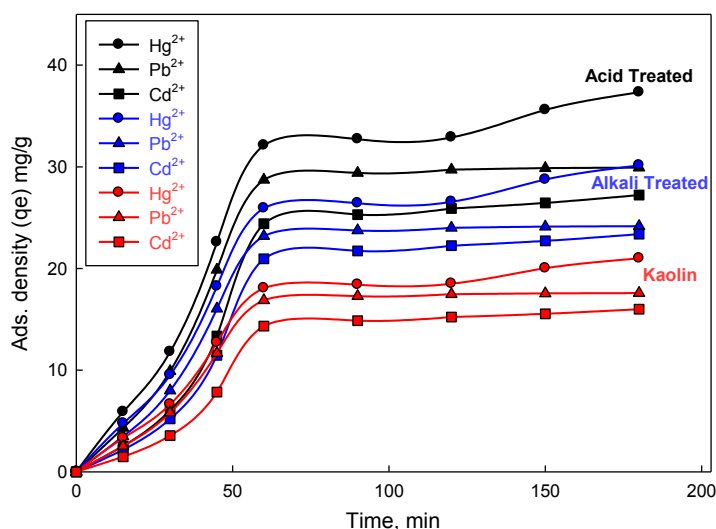


Fig.3. Effect of contact time on metal ion adsorption onto treated kaolins.

In order to investigate the mechanism of adsorption, particularly potential rate-controlling step, the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intra-particle diffusion model were used to test the dynamic experimental data.

3.2.2.1. Pseudo-first-order model

The integral form of the model generally expressed as [42–44]

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303} \right) t$$

where q_t and q_e represents the amount of metal ion adsorbed (mg/g) at any time t and at equilibrium time respectively and K_1 represents the adsorption first-order rate constant (min^{-1}). A plot of $\log(q_e - q_t)$ versus time, t , gives the value of K_1 and also q_e can be calculated.

Fig. 4 shows plot of $\log(q_e - q_t)$ versus t gives a straight line as per pseudo-first-order adsorption kinetics which allow computation of the rate constant K_1 with high linear regression coefficient (R^2) suggest that the metal ion adsorption experiment follows pseudo first-order kinetics. Moreover pseudo-first-order kinetic model predicts a closer value of the equilibrium adsorption capacity as the experimental value and hence it gives the applicability of this model.

3.2.2.2. Pseudo-second-order model

The adsorption data was then analyzed in terms of pseudo second-order mechanism, described by [42–45]

$$\frac{dq}{dt} = K_2(q_e - q_t)^2$$

where K_2 is the pseudo-second-order rate constant (g/mg min).

Integrating and applying boundary conditions $t=0$ to $t=t$ and

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e} \right) t$$

Thus the rate constant K_2 , initial adsorption rate h and predicted q_e can be calculated from the plot of t/q versus time t . Fig.5 shows plot of t/q versus time t gives a straight line as per pseudo-second-order adsorption kinetics which allows computation of the rate constant K_2 with very poor linear regression coefficient (R^2) of 0.17–0.80. Moreover pseudo-second-order kinetic model predicts a much higher value of the equilibrium adsorption capacity than the experimental value and hence it gives the inapplicability of this model.

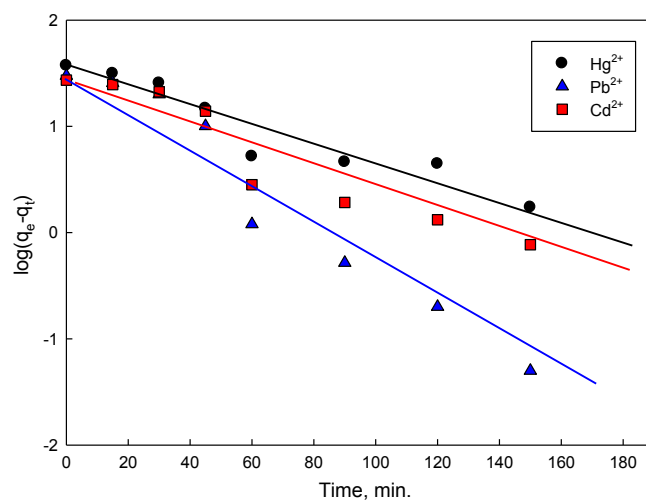


Fig.4. Plotting of Pseudo-first order model.

Table 2:Pseudo-first-order parameters

Item	Kaolin			Alkaline-Kaolin			Acid treated Kaolin		
	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺
R ²	0.9128	0.9595	0.9212	0.9119	0.9598	0.9162	0.9119	0.9599	0.9160
Intercept	1.3062	1.4149	1.2678	1.4625	1.5548	1.4266	1.595	1.493	1.473
Slope	-0.0089	-0.0199	-0.0118	-0.0089	-0.0199	-0.0116	-0.008888	-0.02000	-0.01158
K ₁	-0.02049	-0.04582	-0.02717	-0.02049	-0.04582	-0.02671	-0.0205	-0.0461	-0.0267
Cal. q _e	20.24	25.99	18.52	29.01	35.87	26.71	39.36	31.11	29.72
Exp. q _e	20.99	17.58	15.99	30.142	24.16	23.37	37.33	29.92	27.22

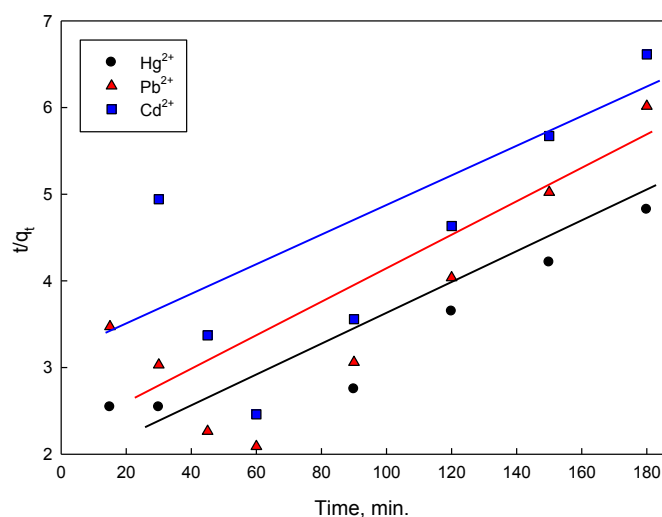


Fig.5. Plotting of Pseudo-second order model.

Table 3: Pseudo-second-order parameters

Item	Kaolin			Alkaline-Kaolin			Acid treated Kaolin		
	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺
R ²	0.8093	0.6913	0.1702	0.8094	0.6912	0.1713	0.8094	0.6911	0.1709
Intercept	2.9358	3.3915	6.4509	2.0450	2.4695	4.4131	1.651	1.994	3.790
Slope	0.0288	0.0322	0.0169	0.0200	0.0234	0.0116	0.01618	0.01891	0.00996
K ₂	2.825×10 ⁻⁴	3.056×10 ⁻⁴	4.427×10 ⁻⁵	1.955×10 ⁻⁴	2.216×10 ⁻⁴	3.048×10 ⁻⁵	1.585×10 ⁻⁴	1.793×10 ⁻⁴	2.619×10 ⁻⁵
Cal. q _e	34.72	31.06	59.17	50.00	42.74	86.21	61.80	52.88	100.36
Exp. q _e	20.99	17.58	15.99	30.14	24.16	23.37	37.33	29.92	27.22

3.2.2.3. Intra-particle diffusion model

Adsorption proceeds in several steps involving transport of the solute molecules from the aqueous phase to the surface of the solid particles and diffusion of the solute molecules into the interior of the pores which is usually a slow process. According to Weber and Morris [46], for most adsorption processes, the uptake varies almost proportionately with $t^{1/2}$ rather than with the contact time and can be represented as follows:

$$q_t = K_{id} t^{0.5} \quad (6)$$

where q_t is the amount adsorbed at time t and $t^{0.5}$ is the square root of the time and K_{id} is the rate constant of intraparticle diffusion.

However these plots (Fig.6) does not fitted with a straight line passing through the origin but also with very poor linear regression coefficients (R_2) indicating the inapplicability of this model and the intra-particle diffusion was not only the rate-controlling step.

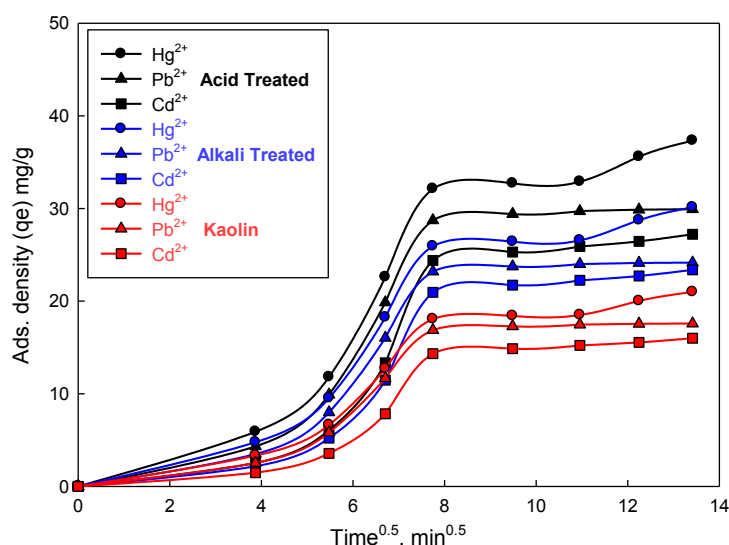


Fig.6. Intra-particle diffusion model

3.2.3. Effect of initial metal ion concentration

The effect of different concentrations of Hg²⁺, Pb²⁺ and Cd²⁺ on the adsorption has been investigated. The amount of metal ions adsorbed is a function of the initial concentration of the adsorbate (metal ions), making it an important factor in effective adsorption. The effect of initial metal ion concentration on the adsorption onto unmodified and modified kaolin clay is shown in Fig.3. It was clear the adsorption capacities of adsorbent increased with the increase in equilibrium metal ion concentration, as the increasing concentration gradient overcomes the resistance to mass transfer of metal ions between the aqueous phase and the adsorbent. A higher concentration in a solution implies a higher concentration of metal ion to be fixed on the surface of the adsorbent [39]. When pore diffusion limits the adsorption process, the relationship between the initial solute

concentration and the rate of adsorption will not be linear[47]. Linearity in Fig.7 proved that the pore diffusion does not limit the adsorption process.

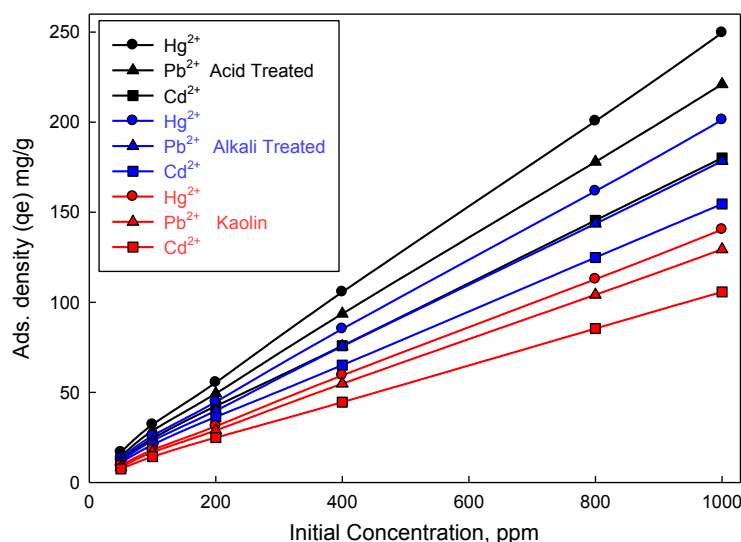


Fig.7. Effect of initial metal ion concentration on adsorption onto kaolins.

The most appropriate method in designing the adsorption systems is to have an idea on adsorption isotherm. Two equilibrium isotherm equations are used to find out the relation between the equilibrium concentrations of the adsorbate in the liquid phase and in the solid phase. These isotherms are as follows.

3.2.3.1. Freundlich isotherm

The Freundlich adsorption isotherm, which assumes that adsorption takes place on heterogeneous surfaces, can be expressed[42, 48] as

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e)$$

Where q_e is the amount of metal ion adsorbed at equilibrium time, C_e is equilibrium concentration of metal ion in solution. K_f and n are isotherm constants which indicate the capacity and the intensity of the adsorption, respectively [42, 48]. The isotherm constants can be calculated from the intercept and slope of plot between $\ln q_e$ and $\ln C_e$.

Fig.8 shows fitting the results on Freundlich isotherm. Freundlich constants i.e. adsorption capacity, K_f and rate of adsorption, n , are calculated from this plot. The value of ' n ' is larger than 1 which indicates the favorable nature of adsorption, Table 4 [50, 51]. Thus, it describes a heterogeneous system characterized by physical adsorption.

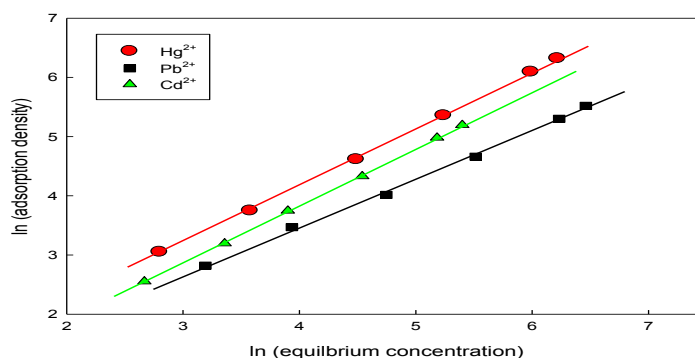


Fig.8. Fitting of results on Freundlich isotherm

Table 4: Freundlich isotherm constants.

Item	Kaolin			Alkali treated			Acid treated		
	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺
R ²	0.9986	0.9985	0.9988	0.9978	0.9979	0.9983	0.9997	0.9981	0.9998
S = 1/n	0.8513	0.8647	0.8362	0.8184	0.8425	0.8112	0.9611	0.8152	0.9678
n	1.17467	1.15647	1.19588	1.22189	1.18694	1.23274	1.04047	1.22669	1.03327
I = ln k _f	-0.6884	-0.8744	-0.949	0.0304	-0.292	-0.302	0.3324	0.2113	-0.040
K _F	0.502379	0.41711	0.38712	1.03086	0.74676	0.73933	1.39431	1.23528	0.96078

3.2.3.2. Langmuir isotherm

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent and once an adsorbate occupies a site, no further adsorption can take place at this site [49]. The linearized form of Langmuir can be written as [42, 48].

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m} \right) \frac{1}{C_e} + \frac{1}{q_m}$$

The Langmuir constants, q_{\max} (maximum adsorption capacity) and K_a can be calculated from the plot between $1/q_e$ versus $1/C_e$. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L , also known as the separation factor, given by [50]

$$R_L = \frac{1}{(1 + K_a C_0)}$$

where K_a is the Langmuir constant and C_0 is the initial metal ion concentration. If the average of the R_L values for each of the different initial concentrations used is between 0 and 1, it indicates favorable adsorption [50].

Fig.9 shows fitting the results on Langmuir isotherm. The Langmuir model fit the data for all metal ions. Thus, it represents a monolayer sorption process onto a homogenous surface as *chemical adsorption*. The maximum adsorption capacity of kaolin, q_{\max} , and constant related to the binding energy of the sorption system, K_a is calculated in Table 5.

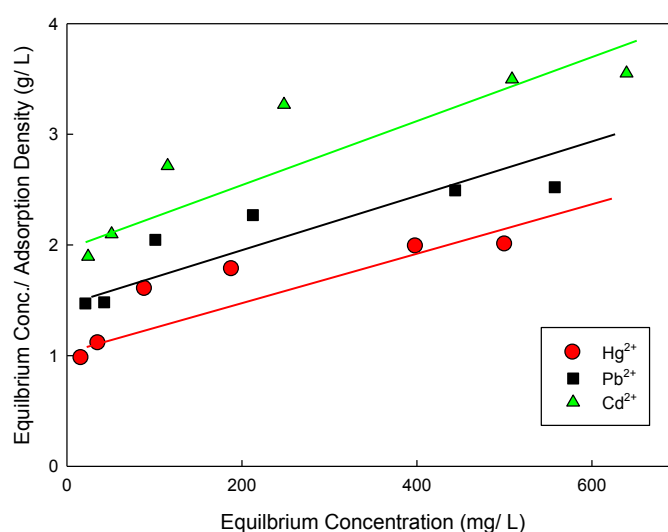


Fig.9. Fitting of results on Langmuir isotherm

Table 5: Langmuir isotherm constants.

Item	Kaolin			Alkali treated			Acid treated		
	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺
R ²	0.7830	0.8035	0.8093	0.7806	0.8021	0.8078	0.7785	0.8007	0.8074
S = 1/q _{max}	0.0024	0.0025	0.0035	0.0020	0.0021	0.0027	0.0019	0.0019	0.0025
I = 1/b.q _{max}	3.6305	4.1453	5.0715	1.9384	2.4649	2.8520	1.1837	1.6100	2.1692
q _{max} (Cal.)	416.6	400.0	285.7	500.0	476.1	370.3	526.3	526.3	400.0
q _{max} (Exp.)	140.4	129.4	105.8	201.24	178.4	154.6	249.6	221.1	180.1
K _a	0.00066	0.0006	0.00069	0.00103	0.00085	0.00095	0.00160	0.00128	0.00115

The dimensionless separation factor or equilibrium parameter, defined as:-

$$R_L = \frac{1}{(1 + bC_0)}$$

Where C₀ (mg/L) is the initial concentration of dye and K_a is Langmuir constant. The value of R_L is indicator of the shape of adsorption isotherm to be favorable or unfavorable. The value of R_L between 0 and 1 indicates favorable adsorption, while R_L=1 suggests unfavorable adsorption and the adsorption process is linear adsorption, while R_L=0 represents irreversible adsorption.

The separation factor, R_L has been calculated from Langmuir plot. It has been found that the range of R_L is 0.9709-0.3846 for this initial metal ion concentration range of 50-1000 ppm which gives favorable adsorption.

Table 6: The dimensionless separation factor

K _a	Kaolin			Alkali treated			Acid treated		
	0.00066	0.0006	0.00069	0.00103	0.00085	0.00095	0.0016	0.00128	0.00115
C ₀	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Cd ²⁺
50	0.9681	0.9709	0.9667	0.9510	0.9592	0.9547	0.9259	0.9443	0.9456
100	0.9381	0.9434	0.9355	0.9066	0.9217	0.9132	0.8621	0.8945	0.8969
200	0.8834	0.8929	0.8787	0.8292	0.8547	0.8403	0.7576	0.8091	0.8130
400	0.7911	0.8065	0.7837	0.7082	0.7463	0.7246	0.6098	0.6793	0.6849
800	0.6545	0.6757	0.6443	0.5482	0.5952	0.5682	0.4386	0.5144	0.5208
1000	0.6024	0.6250	0.5917	0.4926	0.5405	0.5128	0.3846	0.4587	0.4651

IV. CONCLUSIONS

The removal of mercury (Hg²⁺) lead (Pb²⁺) cadmium (Cd²⁺) ions from aqueous solution by kaolin and its modified forms has been investigated. The following conclusions can be drawn based on this investigation:

- The adsorption characteristics of metal ions are strongly affected by the pH, initial metal ion concentration and modification type. It has been found that the amount of metal ion adsorption increases with initial metal ion concentration, contact time and solution pH. The maximum adsorption was achieved by acidic treated kaolin followed by alkalitreated kaolin.

- It has also been found that the amount of adsorption increases with increasing contact time at all initial metal ion concentrations and equilibrium is attained within 60 min. The adsorption process is strongly dependent on the pH of the medium with enhanced adsorption as the pH turns from acidic to alkaline side till precipitation sets in.
- The adsorption capacity of kaolin and modified kaolins for metal ions was as follows: $Hg^{2+} > Pb^{2+} > Cd^{2+}$. These results may be due to that the fluctuation motion of $Hg^{2+} > Pb^{2+}$ and that which is greater than Cd^{2+} .
- Kinetic experiments clearly indicate that adsorption of Hg^{2+} , Pb^{2+} and Cd^{2+} ions on untreated and treated kaolins two steps process: a rapid adsorption of metal ions to the external surface followed by intraparticle diffusion into the interior of adsorbent. Overall the kinetic studies showed that the metal ions adsorption process followed pseudo-first-order kinetics. The various pseudo-first-order kinetic parameters including rate constant are determined.
- Langmuir and Freundlich equations both are applicable to describe the adsorption of Hg^{2+} , Pb^{2+} and Cd^{2+} ions on untreated and treated kaolins. The constant value, R_L (low separation factor) in Langmuir isotherm gives an indication of favorable adsorption.

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